

Reduction of Ingestion Exposure to Trihalomethanes Due to Volatilization

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Ingestion of tap water is one of the principal exposure pathways for disinfection byproducts (DBPs). One major class of DBPs, trihalomethanes (THM), are highly volatile, and volatilization will tend to lower ingestion exposures. This study quantifies volatilization rates of the four THM species that occur while drinking tap water, specifically, losses during the preparation, storage, and serving of water. A mass transfer model based on two-resistance theory and quiescent conditions is presented, and parametrizations of all variables are provided. Volatilization rate constants are estimated in experiments representing common patterns of tap water consumption, i.e., storage of tap water in pitchers, pouring, and serving in glasses and mugs at temperatures from 4 to 100 °C. Predicted and experimental results show comparable loss rates for the four THMs. Observed volatilization rates declined exponentially, as expected, and greatly exceeded model predictions that assumed quiescent conditions in the liquid. Loss rates increased with temperature and mixing that resulted from temperature gradients and air currents. Overall, storage, pouring, and serving of tap water at temperatures below 30 °C caused minor (<20%) volatilization of THMs. Rapidly heating water to 60 or 80 °C also is not expected to result in significant volatilization. However, volatilization losses approached 75% when water was boiled even for brief periods of time and reached 90% when boiled water was poured and served. For the typical adult who drinks nearly half of their water as hot beverages, volatilization will reduce ingestion exposures of THMs by nearly a factor of 2. To account for these losses, exposure estimates for THMs and other volatile chemicals should separate the consumption of heated and unheated tap water.

Introduction

Understanding exposures to disinfection byproducts (DBPs) that result from water chlorination has been a priority since the finding that chloroform and other trihalomethanes (THMs) can be formed during chlorination (1, 2). Human exposures to DBPs in drinking water occur by ingestion, inhalation (3–5), and skin permeation (6, 7). Inhalation exposures may result from volatilization of THMs (and other contaminants) that are dissolved in tap water. Each of these exposure pathways may be important under some circumstances (8–13). Factors that control exposures include the occurrence and distribution of the chemicals in air, water,

soil, and other media; household characteristics such as exchange rates and ventilation; and activity patterns and lifestyle of the individual such as diet, hobbies, and bathing frequency (14). Several studies have integrated volatilization and exposure models (4, 13–15).

Compounds with a Henry's law constant (*H*) exceeding 0.001 atm·m³/mole or 0.1 (mass/volume)_{gas}/(mass/volume)_{liquid} are considered to be highly volatile (16). The THMs exceed or approach this value, i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform (CHCl₃, CHCl₂Br, CHClBr₂, and CHBr₃) have Henry's law constants at 20 °C of 0.0034, 0.0013, 0.00081, and 0.00058 atm·m³/mole, respectively. *H* increases with temperature, and at 30 °C even CHBr₃ would be considered highly volatile. Volatilization of THMs, especially CHCl₃, has been characterized for indoor swimming pools and spas (10, 17, 18), showers (12, 19–23), washing machines (24), and kitchen sinks (25). Volatilization rates depend on the specific DBP (concentration, aqueous solubility, Henry's law constant, vapor pressure, diffusivity constant), the presence of modifying materials (adsorbents, organic films, electrolytes, and emulsions) (16), water usage, water temperature (26), air flow and exchange, shower head or atomizer design (droplet size, dispersion, etc.), and activity patterns (frequency and duration of showers, baths, etc.). The knowledge base for volatilization from most indoor sources is rather limited (25), and it is difficult to predict mass transfer coefficients on the basis of laboratory studies (16). Thus, additional measurements of mass transfer coefficients are needed (14).

This study examines the volatilization of THMs from tap water that occurs during the direct consumption of tap water. Volatilization reduces the aqueous phase concentration, thus decreasing ingestion (and skin permeation) exposures. Surprisingly, no study was found that characterized volatilization losses from water served in an ordinary pitcher, glass, or mug. Nor has any study examined the effect of temperature on these losses, although water is served from near freezing to boiling temperatures. A model is assembled to predict volatilization losses from tap water consumption, and critical model parameters are estimated in experiments that represent several common patterns of tap water consumption.

Model Development

A one-dimensional volatilization model, based on mass balance and two-resistance theory, is developed from work examining volatilization from quiescent and turbulent waters in both natural and engineered systems (27–30). Parametrizations presented allow estimates of volatilization rates for each THM at a specified temperature.

The mass balance for a contaminant in water with loss due to volatilization can be expressed as

$$d(CV)/dt = -K_{OL}(C - C_G/H)A \quad (1)$$

where *C* = concentration in water (μg/cm³), *V* = volume of water (cm³), *t* = time (s), *K_{OL}* = overall mass transfer coefficient (cm/s), *C_G* = concentration in air adjacent to the water (μg/cm³), *H* = Henry's law constant ((mass/volume)_{gas}/(mass/volume)_{liquid}), and *A* = interfacial surface area between water and air (cm²) (25). If the concentration in air *C_G* is negligible, water volume *V* is constant, and the contaminant mass in the water is finite and unreplenished, the concentration remaining in water, *C_t* (μg/cm³), declines exponentially

$$C_t = C_0 \exp(-kt) \quad (2)$$

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where C_0 is the initial concentration ($\mu\text{g}/\text{cm}^3$) at $t = 0$, and k = volatilization rate constant (1/s) defined as

$$k = K_{OL}A/V = K_{OL}/h \quad (3)$$

where h = water depth (cm). Equation 3 applies to quiescent conditions. It is not applicable if the fluid is mixed due to pouring, boiling, or other conditions.

Mass transfer coefficient K_{OL} may be estimated using two-resistance theory assuming that the bulk air and water phases are well mixed and that the two phases are separated by thin and quiescent films of air and water in which transport takes place by molecular diffusion (31). If so, K_{OL} can be expressed as

$$1/K_{OL} = 1/K_L + 1/(HK_G) \approx \delta_L/D_L + \delta_G/(HD_G) \quad (4)$$

where K_L and K_G are liquid and gas-phase mass transfer coefficients (cm/s), respectively. Under equilibrium conditions, these terms can be expressed in terms of diffusion coefficients D_L and D_G (cm^2/s) and film thickness δ_L and δ_G in water and air, respectively (cm). While usually empirically determined, K_L and K_G may be scaled from a reference substance (32), based on diffusion coefficients (20) or critical (molecular) volumes (28). Resistance in either the water or air phase generally dominates mass transfer (16). If $H K_G \gg K_L$, as generally applies to highly volatile compounds, then the gas-phase resistance is negligible and $K_{OL} \approx K_L$. For lower volatility compounds, both gas and liquid-phase resistances must be considered.

Under ideal quiescent conditions, molecular diffusion is the only driving force, and the entire water depth may be considered as the liquid film. For such conditions, Peng et al. (29) approximates a solution to Fick's second law

$$k \approx \pi^2/(4h^2)D_L \quad (5)$$

which can be used in eq 2. The diffusion model and the quiescent assumption represents an extreme condition, yielding volatilization rates that represent a lower bound. Volatilization rates may be much higher with mixing of the liquid (29, 30) and/or rapid air velocity above the liquid if air-phase resistance is important (27, 32).

Parametrization of Liquid-Phase Resistance. Diffusion coefficients for a compound in water, D_L , may be measured directly or estimated as

$$D_L = k_C D_{\text{ref}}(T/T_{\text{ref}})(\mu_{L,\text{Tref}}/\mu_{L,T}) \quad (6)$$

where k_C = ratio of the diffusion rate of the target compound to that of a reference substance, D_{ref} = diffusion coefficient (cm^2/s) for a reference substance measured at temperature T_{ref} (K), T = temperature of concern (K), and $\mu_{L,\text{Tref}}$ and $\mu_{L,T}$ = viscosity of water at the reference and test temperatures, respectively (poise). The reference compound is often O_2 , which has a diffusion coefficient of $2.24 \times 10^{-5} \text{ cm}^2/\text{s}$ at 20°C (33). Values of k_C for the THMs are 0.46, 0.41, 0.43, and 0.41 for CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 , respectively (33).

Water viscosity is a strong function of temperature, estimated as follows (34):

$$\log \mu_L = \begin{cases} 1301/[998.333 + 8.1855(T - 293) + 0.00585(T - 293)^2] - 3.30233 & (T < 20^\circ\text{C}) \\ [1.3272(293 - T) - 0.001053(T - 293)^2]/(T - 168) - 1.99913 & (T > 20^\circ\text{C}) \end{cases} \quad (7)$$

Parametrization of Gas-Phase Resistance. The diffusion coefficient in air may be obtained from the gas-phase Schmidt number Sc_G (dimensionless)

$$D_G = \mu_G/(\rho_G Sc_G) \quad (8)$$

where ρ_G = air density (g/cm^3) and μ_G = viscosity of air (poise) (14). Temperature adjustments use the ideal gas law for density

$$\rho_G = 0.001293(273.15/T)(P/101.3) \quad (9)$$

where P = pressure (kPa). The viscosity of air is estimated as (35)

$$\mu_G = 0.0001708(T/273.15)^{1.5} 393.396 / (T + 120.246)(T/101.3) \quad (10)$$

The temperature dependence of H is

$$H \sim T^{-1} 10^{-B/T} \quad (11)$$

where B = temperature correction coefficient. Values of B are 1930, 2050, 2050, and 2170 for CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 , respectively (33). (Note that available literature values of H vary with about a 25% range.)

Air velocity above the water surface and surface disturbances influence air film thickness δ_G . Air velocities in buildings vary spatially and temporally, thus, the film thickness is unknown. In the following, a range of values is tested.

Experimental Section

Exposure Scenarios. Experiments were designed to mimic several tap water drinking patterns, including tap water stored in pitchers and served in glasses at chilled and room temperatures, and tap water heated to boiling and served in a mug, representing the preparation of tea or other hot beverage. Effects of glass shape (tall, wide-mouth), temperature (4 to 100°C), and storage time (0 to 4 h) were evaluated. THM losses due to water preparation (heating, cooling), serving (pouring), and storage in the serving container were also characterized.

Experiments were conducted at a variety of temperatures: chilled (4 to 16°C), room temperature (25°C), warm (30°C), and heated (40, 60, 80, and 100°C). All experiments used distilled chlorine-free water. The THM stock solution (2 mg/mL of each THM) was diluted in a filled 4 L black bottle to obtain the test mixture containing $100 \mu\text{g}/\text{L}$ of each THM compound and then transferred to a typical covered water pitcher (Rubbermaid, capacity = 2.34 L, filled to 1.96 L, height = 21.7 cm, dia = 12.2 cm, material = resin) and used to fill glasses or mugs. In experiments at elevated temperatures, the test mixture was transferred directly to a kettle (described below).

To investigate THM losses that occur at the tap and during preparation but before serving, concentrations were measured in the stock solution and compared to samples taken immediately after filling the beverage container. The experimental procedure portrayed the filling of a pitcher from the tap (transfer from the black bottle in the experiment) and then the filling of a glass from the pitcher. In both cases, water transfers were done quickly (3–5 s) and at a minimal (2 cm) pouring height. No aerator or screen was used. The determination of the more gradual losses from standing water in glasses and coffee mugs is described below.

In the 25 and 30°C experiments, the test mixture was transferred to the pitcher and then poured into glasses. Typical full-size "tall" glasses (volume = 350 mL, mouth dia = 6.0 cm, depth = 12.4 cm, all inner dimensions) were used,

both full and half-full. In addition, flared wide-mouth glasses (volume = 400 mL, mouth dia = 9.5 cm, depth = 8.3 cm) were used. Both types of glasses were made of clear glass. The 30 °C experiments maintained test temperatures using a water bath into which glasses were placed, submerging the bottom 3–4 cm of the glasses. While the use of the water bath in this experiment does not portray serving conditions, it allows the use of a constant elevated temperature.

Chilled water experiments were designed to portray tap water stored in a refrigerator and then served in insulated glasses. The test mixture in the closed pitchers was refrigerated to 4 °C. Then, the same tall glasses were filled from the pitchers. To mimic the insulated beverage containers often used for cold drinks, glasses were covered with two layers of bubble wrap.

Boiling temperature experiments simulated the making of tea or other hot drink. An electric kettle (600 W; capacity = 1.425 L, material = coated steel) was filled with 1.05 L of the test mixture and heated to 60, 80, and 100 °C. Water samples were collected directly from the kettle at these three temperatures. In addition, boiled water was poured into typical ceramic coffee mugs (volume = 250 mL, mouth diameter = 7.3 cm, depth = 8.7 cm) and sampled periodically for 1 h.

Glasses and mugs were placed on a table in the laboratory, and in most cases, samples were taken 0, 10, 30, 60, 120, and 240 min after filling. Thirty milliliter samples were collected using a 50 mL glass syringe (Hamilton) with a long stainless 19 gauge needle. To provide a representative sample, the sample was split between the top, middle, and bottom of each glass or mug. Each mug or glass was sampled only once, as sampling is likely to introduce mixing. Each experiment was done in duplicate. A single experimental condition (one style glass at one temperature with 2 replicates) required the collection and analysis of 14 samples from 12 glasses (for 6 sample times) and 2 black bottles (for presample measurements).

During the study period, the laboratory temperature was maintained at 25 °C, the relative humidity varied from 34 to 66%, and the air velocity immediately above the table where glasses and mugs were filled was 0.17 to 0.33 m/s as measured using a hot-wire anemometer (Alnor 8565, Skokie, IL). Chilled or heated samples gradually approached room temperature; water temperatures in these experiments were measured periodically.

Sample Analysis and Calibration. THMs were analyzed using a liquid–liquid extraction method adopted from EPA 551 and APHA 6232B (36). The 30 mL sample was extracted with 2 mL of pentane (THM Grade, Sigma-Aldrich), from which 1 μ L was injected splitless into a gas chromatograph (GC) (Varian 3700, Mountain View, CA) equipped with an electron capture detector (ECD). The GC used an injection temperature of 200 °C; initial column temperature of 35 °C for 5 min, ramped at 20 °C per min to 180 °C and then held for 3 min; and ECD temperature of 280 °C; a 30 m \times 0.53 mm wide bore capillary column with 0.5 μ m SPB-5 coating (Supelco, Supelco Park, Bellefonte, PA); N₂ carrier gas at 25 cm/s; and N₂ makeup gas at 30 mL/min. This method achieved detection limits from 0.01 to 0.07 μ g/L, recoveries from 86 to 113%, and reproducibility from 2.7 to 16.6%.

THM standards included both a mixture THMs prepared at 2000 μ g/mL each in acetone (EPA 551A Halogenated Volatile Mix, Supelco) and neat standards of the same compounds (Supelco, except CHCl₃ from Fluka). Stock solutions (200 μ g/mL) were prepared in methanol and further diluted to prepare calibration standards.

To confirm results, each experiment was performed in duplicate, approximately 20% of the GC-ECD analyses were repeated, and blank water samples were collected and

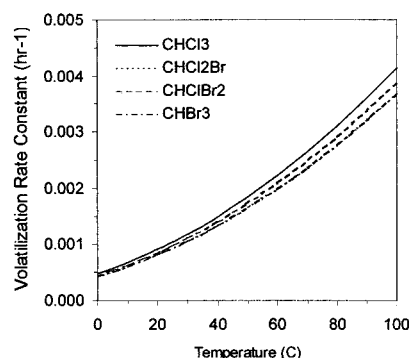


FIGURE 1. Predicted volatilization rate constants for nominal case (e.g., 10 cm deep water layer, 1 cm thick air film, 1 cm thick water film) as a function of temperature. Lines for CHCl₂Br and CHBr₃ overlap.

analyzed. Almost all coefficient of variations were <10%. THMs were not detected in any blank.

Data Analysis. Estimates of losses during water preparation (heating, cooling) and pouring into the serving container were obtained by comparing prepared concentrations in the black bottle (100 μ g/L) with concentrations in the container immediately after filling ($t = 0$). Duplicate measurements were averaged. Errors were estimated as standard deviations using Gaussian quadrature and the standard deviation of replicate samples. Results were expressed as percentage change from the stock solution.

Empirically derived volatilization rate constants were determined by fitting k in eq 2 to experimental results for each compound and minimizing the squared residuals. It was assumed that $C_G = 0$ and that negligible evaporation of water occurred so that V and h were constant. Both k and C_0 were fitted parameters, thus, THM losses from water preparation (heating or cooling) or serving (pouring) are not included in the estimate of k . Theoretical predictions from the two-resistance model were compared to experimental results.

Results

Model Predictions. Figure 1 shows volatilization rate constants predicted for a typical beverage container, i.e., a 10 cm column of water. The air film thickness δ_G is assumed to be 1 cm; however, results were insensitive to this parameters. Volatilization rates are a strong function of temperature, e.g., the average rate for the four THM species at 0 °C (0.000443 h⁻¹) doubles at room temperature (0.000897 h⁻¹ at 22 °C) and quadruples at 100 °C (0.00384 h⁻¹). The more volatile THMs have larger rate constants, but differences among the THMs are small, i.e., <17% between the most (CHCl₃) and least (CHBr₃) volatile compounds. These results apply for a 10 cm depth of quiescent water and a 1 cm air film. Resistance in water phase accounts for >99% of the total mass transfer resistance. Consequently, volatilization rate constants are inversely proportional to the square of the water depth. Decreasing the air film thickness to 0.1 cm makes no difference in k , while increasing the thickness to 10 cm (an unlikely depth) decreases k by only 0.1%. Thus, even very thick air films cause only a minor reduction in THM volatilization rates. Air film thicknesses on the order of 0.1 to 1 cm are reasonable in typical indoor settings. Thicker air films may occur if the water surface is sheltered and air currents are minimal.

Two-resistance mass transfer theory shows that the volatilization rate constant is inversely proportional to the film thickness. For air and water film thickness of 1, 0.1, and 0.01 cm, $k = 0.00363$, 0.0363, and 0.363 h⁻¹, respectively, for a 10 cm deep container at 22 °C and the average of the four

TABLE 1. Average Percentage Losses in THM Concentrations Measured in Glasses and Mugs from Original Stock Solution^a

THM	chilled water 4 °C		room temp 25 °C		heated in kettle 60 °C		heated in kettle 80 °C		heated in kettle 100 °C		heated, poured 100 °C	
	av	(SD)	av	(SD)	av	(SD)	av	(SD)	av	(SD)	av	(SD)
CHCl ₃	-4.3	(4.7)	2.9	(7.0)	14.7	(6.0)	29.6	(12.0)	81.0	(5.7)	85.1	(5.4)
CHCl ₂ Br	-1.4	(2.8)	2.3	(1.6)	10.5	(4.1)	24.3	(9.5)	73.0	(7.2)	79.8	(4.7)
CHClBr ₂	-1.9	(2.5)	1.5	(5.5)	6.7	(5.5)	17.3	(5.3)	62.3	(7.2)	71.6	(4.7)
CHBr ₃	-3.1	(2.7)	1.8	(5.5)	12.4	(9.1)	16.2	(6.0)	58.0	(10.4)	62.9	(5.7)
av	-2.7	(3.2)	2.1	(4.9)	11.1	(6.2)	21.9	(8.2)	68.6	(7.6)	75.3	(5.1)

^a Pouring losses shown for 4 and 25 °C experiments. Pouring plus heating losses for other experiments. Standard deviation in parentheses.

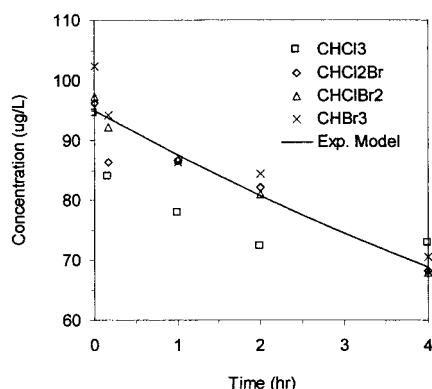


FIGURE 2. Trends of THM concentrations in wide mouth glasses at 25 °C. Average determinations for four THMs at each averaging time shown as points. Trend line (exponential model) uses average coefficient across four THMs.

THMs. These values are 4 to 400 times greater than those estimated using eq 5, which assumed that the entire 10 cm water layer is quiescent. Air phase resistances ranged from 0.07% (CHCl₃) to 0.47% (CHBr₃) of the total resistance. As mentioned, the film thicknesses are unknown, but water phase resistance dominates under all conditions.

Losses from Pitcher to Glass and from Boiling. Volatilization losses due to pouring water from the black bottle into the pitcher and then from the pitcher into the serving container are shown in Table 1. For chilled and room-temperature water, losses were negligible (−4.3 to 2.9%). (Negative losses, which indicate concentrations after serving were higher than the stock solution, are not statistically meaningful.) While greater volatilization would be expected by filling the glass more slowly and increasing the pouring height, only small losses are anticipated by pouring water at or below room temperature.

Heating water to boiling, which required 12.5 min in the kettle, volatilized an average of $69 \pm 8\%$ of the THMs in the kettle, and slightly more, $75 \pm 5\%$, after the boiling water was transferred to the mug (Table 1). However, heating to lower temperatures did not result in large losses. For example, heating to 60 °C, which required about 7 min in the electric kettle, released $15 \pm 6\%$ of the THMs. Heating to 80 °C, which required 9.5 min, released $22 \pm 8\%$. CHCl₃ losses at 60 to 100 °C were 13 to 33% higher than the THM average, while CHClBr₂ and CHBr₃ losses were 5 to 40% lower. (Measurements of CHBr₃ at 60 °C seem anomalously large and are excluded from these statistics.) Volatilization rates during heating of water may be influenced by the type of kettle (e.g., size, covered, uncovered), boiling time, pouring time and height, and possibly other factors.

Losses from Serving Containers at Room and Warm Temperatures. Typical trends of THM concentrations in the room temperature (25 °C) experiment are shown in Figure 2. Loss rates for the THMs were similar and small (Table 2). For example, over the 4-h period, losses were only 18% for

the full tall glass, 24% for half-filled glasses, and 28% for the wide-mouth glasses (average of the 4 THMs). The exponential model (eq 2) fit experimental results reasonably well, with most R² values from 0.6 to 0.9. Model fit was poorest for the tall glass experiments at 25 °C, largely because the small concentration changes (16 to 23%) had the effect of increasing relative errors. At 25 °C, the average volatilization rate ($0.048 \pm 0.005 \text{ h}^{-1}$) in the full tall glass was between that of the half-full tall glass and the wide-mouth glass. As expected, losses were more rapid from the wide-mouth glasses. Still, THMs losses would be minimal for water served under quiescent or near-quiescent conditions and consumed within a few hours, e.g., if the water is drunk within 1 h of pouring, THM concentrations would be reduced by only 5 to 12%.

Increasing and maintaining the water temperature at 30 °C increased volatilization rates 3-fold (Table 2). However, theoretical predictions gave only a slight (15%) increase in *k* from 25 to 30 °C. The slightly elevated temperature, 5 °C above ambient, was maintained by warming the bottom of the glass in a water bath. The temperature gradient between the water bath and water/air interface helps to induce convective currents that promote mixing. As a result, volatilization rates at 25 and 30 °C differed significantly and also departed from predictions that assumed quiescent conditions. While the 30 °C experiments do not reflect typical activity patterns, they show the influence of mild mixing that might occur from gentle stirring, air currents, etc.

Differences in volatilization rates among the THMs in 25 and 30 °C experiments were not pronounced. At 25 °C, the coefficients for the four THMs were largely indistinguishable. At 30 °C, coefficients for CHCl₃ were 18 to 24% above the average, and coefficients for CHClBr₂ and CHBr₃ were 7 to 14% lower (excluding CHBr₃ in the full tall glass which appeared somewhat high).

Glass Shape and Content. With respect to glass type, both 25 and 30 °C experiments showed the same trend, i.e., volatilization rates were smallest in the full tall glass, intermediate in the half-full tall glass, and largest in the wide-mouth glass. For the wide-mouth glass, however, concentration trends over the 4-h period did not fit the one-dimensional exponential model. Observed THM levels decreased rapidly over the first hour, and then the rate of decrease lessened for the remainder of the experiment. This pattern, which was not observed in other experiments, may arise due to the container's geometry. Flaring increases the liquid/air surface area, leading to initially rapid volatilization. At later times, volatilization rates reflect losses throughout the water column, including deeper layers where the THM reservoir is smaller due to the reduced cross-section. To better account for the observed trends, two estimates of volatilization rate *k* are provided in Table 2. The first used all of the data (to 4 h); the second used only observations from the first 1 h (at 0, 10, 30, and 60 min). The latter is significantly higher (average of 60% for all four THMs and both temperatures), as expected given the geometrical configuration of the flared glass.

Chilled Water. Theoretically, cooler temperatures should lower the mass transfer rates. Figure 3 plots concentration

TABLE 2. Estimated Volatilization Rate Constants (h^{-1}) in Room-Temperature Experiments at 25 and 30 °C^a

temp (°C)	THM	tall glass – full			tall glass – half full			wide mouth glass – full ^b			wide mouth glass – half		
		k	(SD)	R ²	k	(SD)	R ²	k	(SD)	R ²	k	(SD)	R ²
25	CHCl ₃	0.055		0.63	0.070		0.77	0.180		0.59	0.079		0.67
	CJCl ₂ Br	0.046		0.53	0.064		0.64	0.110		0.30	0.077		0.70
	CJC;Br ₂	0.047		0.47	0.063		0.76	0.108		0.61	0.085		0.87
	CHBr ₃	0.044		0.33	0.062		0.56	0.140		0.71	0.084		0.79
	av	0.048	(0.005)	0.49	0.065	(0.004)	0.68	0.135	(0.034)	0.55	0.081	(0.004)	0.76
30	CHCl ₃	0.183		0.69	0.248		0.83	0.411		0.62	0.316		0.79
	CHCl ₂ Br	0.135		0.65	0.205		0.90	0.427		0.80	0.254		0.81
	CHClBr ₂	0.142		0.74	0.177		0.90	0.392		0.82	0.224		0.79
	CHBr ₃	0.158		0.85	0.193		0.89	0.332		0.76	0.224		0.82
	av	0.154	(0.021)	0.73	0.206	(0.030)	0.88	0.391	(0.042)	0.75	0.255	(0.044)	0.81

^a Standard deviation in parentheses. R² shows model fit to observations. ^b Uses only first hour of data.

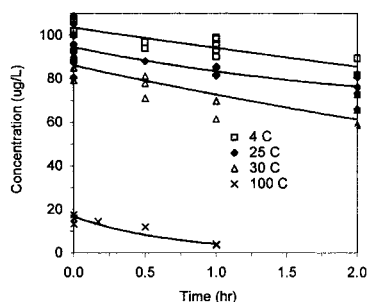


FIGURE 3. Trends of CHCl₃ concentrations from water served in tall glasses at 0, 25, and 30 °C and from coffee mug at 100 °C. Stock solution (prior to heating or cooling) prepared at 100 µg/L. Trend lines based on exponential model. Based on 2 replicates at each time and temperature. (Symbols show individual data points, but overlap is not shown.)

TABLE 3. Estimated Volatilization Rate Constants (h^{-1}) for Chilled and Boiled Water^a

THM	initial temp = 4 °C			initial temp = 100 °C		
	k	(SD)	R ²	k	(SD)	R ²
CHCl ₃	0.088		0.77	1.50		0.86
CHCl ₂ Br	0.076		0.78	1.52		0.82
CHClBr ₂	0.080		0.75	1.41		0.80
CHBr ₃	0.080		0.84	1.40		0.85
av	0.081	(0.005)	0.78	1.46	(0.06)	0.83

^a Standard deviation in parentheses. R² shows model fit to observations.

trends for CHCl₃ in water at 4, 25, 30, and 100 °C. The intercepts on the figure represent the initial losses in THM concentrations (quantified in Table 1), a result of transfers from the 100 µg/L test solution to the glass or mug. Surprisingly, concentrations at 4 °C appear to decline faster than those at 25 °C. The decline at 30 and 100 °C is definitely faster (discussed later). The average volatilization rate for chilled water ($0.081 \pm 0.005 \text{ h}^{-1}$) is nearly twice that observed at 25 °C in the same style glass ($0.048 \pm 0.005 \text{ h}^{-1}$, Table 3). Over the 2-h period of these experiments, THM losses from the chilled water averaged $16.5 \pm 1.2\%$, and water temperatures in the (insulated) glass increased from 4 °C to 13 °C at 1 h and to 17 °C at 2 h. Like the 30 °C experiment, the water–air temperature gradient in the chilled water experiment appears to promote mixing that more than compensates for the lower temperature.

Boiling Water. As seen earlier, boiling greatly reduced THM concentrations. THM losses continued as hot water sits in the cup prior to consumption. Volatilization rate constants for boiling water in coffee mugs were determined

using samples taken 0, 10, 30, and 60 min after filling the mug (Table 3). THM losses were rapid, e.g., the average volatilization rate constant was $1.46 \pm 0.06 \text{ h}^{-1}$, about 30 times that seen at 25 °C. The predicted rate constant is 0.0548 h^{-1} , about 20 times higher than at 25 °C. The high temperature in the mug is likely to induce mixing that accounts for the more rapid volatilization. Like earlier experiments, volatilization rates for the four THMs were similar. The rates in Table 3 reflect changing water temperatures, i.e., 92 °C after pouring, 52 °C at 0.5 h, and 40 °C at 1 h.

Results in Tables 1 and 3 can be used to estimate the total loss of THMs from tea or coffee preparation and serving, e.g., heating tap water to boiling and serving after a “steeping” and cooling period of 0.5 h, would be 87.5% (75% loss in boiling and filling the mug and 50% loss of the remainder in serving).

Comparison to Model Predictions. Table 4 lists observed and predicted volatilization rate constants for the different experiments. Because differences between the THM species were small, only the average k among the four THMs is shown. Since temperatures changed in the chilled and boiling water experiments, predictions are shown for temperatures spanning experimental conditions, and the observed/predicted ratio is computed using the average k predicted over these temperatures.

Using the quiescent model, volatilization rate constants were greatly overpredicted (factor of 28 to 295 times). The overprediction results from mixing in the containers, due in part to air currents that were present in every experiment. In addition, nonisothermal conditions in the 4, 30, and 100 °C experiments were likely to produce a degree of convective mixing. In contrast, predictions assumed an ideal quiescent liquid in which diffusion governs transport throughout the entire water column depth. Effects of temperature are limited to changes in water viscosity, diffusion coefficients, and Henry’s law constant. Underprediction was smallest (~100 times) in the isothermal (25 °C) and the half-full glass (28 to 77 times) cases. In these experiments, mixing in the water was expected to be at a minimum, and the half-full glass should provide some sheltering that reduces the air velocity above the water surface. These effects are multiplicative, i.e., the sheltered isothermal experiment showed the smallest degree of overprediction (28 times).

Table 4 also shows estimated water and air film thicknesses (assumed to be equal) that matched the observed volatilization rate constant. In the 25 °C experiments where mixing is minimized, the film thicknesses were 0.05 to 0.08 cm. In the nonisothermal experiments, film thicknesses were considerably smaller, about 0.02 cm. While approximate, these relatively thin films further demonstrate the significance of mixing throughout the 6.2 to 14.5 cm deep water column in the laboratory experiments.

TABLE 4. Comparison of Observed and Predicted Mass Transfer Coefficients^a

container	water column height (cm)	temp (°C)	obs k (h ⁻¹)	quiescent model		fitted air and water film thickness (cm)
				pred k (h ⁻¹)	ratio obs k/pred k	
tall glass	14.5	4	0.081	0.00024	276.9	0.018
		8		0.00028		0.020
		16		0.00036		0.026
		av		0.00029		0.021
tall glass	14.5	25	0.048	0.00046	103.9	0.056
tall — half full	6.2		0.065	0.00232*	27.9	0.081*
wide-mouth	8.5		0.135 ^b	0.00133	100.8	0.047
tall glass	14.5	30	0.154	0.00052	295.1	0.020
tall — half full*	6.2		0.206	0.00266*	77.4	0.024*
wide-mouth ^b	8.5		0.391 ^b	0.00152	257.6	0.013
coffee mug	6.2	100	1.5	0.00997	266.2	0.017
		80		0.00749		0.012
		60		0.00536		0.009
		40		0.00358		0.006
		av		0.00548		0.011

^a Quiescent model uses 1 cm air thickness except for * which uses 6.2 cm. Fitted air and water film thicknesses are equal as indicated except for * which uses 6.2 cm for air film thickness. ^bBased on first hour of data only.

The exponential model provided a good fit to observations, except for experiments using the flared glass. In this case, the one-dimensional model does not provide an appropriate geometrical match, since the flared glass leads to both fast and slow volatilization processes from upper and lower depths, respectively.

Discussion

Tap water consumption has been used as a surrogate for DBPs exposures in epidemiological studies aimed at understanding dose-response relationships (37), and ingestion exposures have driven risk assessments and standard setting activities. Experimental results indicate that volatilization occurring during tap water consumption will decrease ingestion exposures for THMs. While volatilization potentially increases airborne concentrations and thus inhalation exposures, small impacts are expected given the few liters of tap water ingested and the large amount of dilution in most indoor environments.

Other Experimental Studies. Volatilization losses of DBPs from drinking activities should follow those of other chemicals in water under near-quiescent conditions. Using radon liberated from tap water, Pritchard and Gesell (38) estimated a transfer efficiency of 30% for drinking and kitchen uses. Howard and Corsi (25) found stripping efficiencies ranging from 1% (acetone) to 48% (cyclohexane) from a kitchen wash basin for flowing and aerated water. Under quiescent conditions, Peng et al. (29) measured volatilization rates of four VOCs from water using small (2 cm dia) vials in a laboratory hood. Experimental results exceeded theoretical calculations by 20 to 30-fold, and volatilization rates were proportional to $h^{1.81}$, smaller than the h^2 implied by eq 5. These differences were likely caused by temperature variation and surface disturbances (due to air currents) that caused dispersion and deviation from ideal quiescent conditions. In larger scale study, Peng et al. (30) showed that mechanical mixing significantly increased the volatilization rates. Earlier, Cohen et al. (39) found transport rates for VOCs with wind-induced mixing to be over 1200 times larger than ideal quiescent conditions. In laboratory tests, Rathburn and Tai (32) showed the dependence of mass transfer coefficients for ethylene dibromide for air temperatures from 20 to 40 °C and wind speeds from 0.3 to 1.7 m/s (faster than expected

indoors); however, both air and water film resistances are important for this compound, unlike the THMs where air film resistance is negligible.

In this study, observed volatilization rate constants greatly exceeded predictions for quiescent conditions. However, general model trends were followed, e.g., volatilization rates increased with shallower containers, flared and wide-mouth glasses, higher temperatures, temperature gradients, and mixing. Given that the liquid phase resistance dominates mass transfer, mixing and dispersion in the water will strongly affect volatilization rates. Experimental results clearly indicate that water in glasses and mugs undergoes mixing under typical serving conditions. The diffusion-based model assuming quiescent conditions throughout the water column can be viewed as a limiting case. Film thicknesses on the order of 0.01 to 0.1 cm, which match experimental findings presented here, will give much higher volatilization losses. In general, empirically derived mass transfer rates must be used to estimate volatilization losses.

Significance of Volatilization Losses. THM losses from tap water in open containers under near-quiescent and near-isothermal conditions will be small, e.g., if the water is drunk within 1 h of pouring, concentrations will be reduced by only 5 to 8%. Somewhat greater losses are expected with mixing that might result from handling of glasses, surface disturbances, stirring, and nonisothermal conditions. Still, storage of water (particularly if the container is mostly sealed and refrigerated), pouring and serving of chilled or warm water, or even rapid heating to 80 °C will not result in large losses. THM losses will be significant, however, if water is boiled or stored in a stirred and open container over a period of hours, corresponding to the preparation of hot beverages (tea, coffee, etc.) and some cooking activities. Losses from boiling water and serving hot beverages depend on several factors, but losses from 80 to 90% appear reasonable based on experimental findings. Both theoretical and experimental results indicate that volatilization rates of CHCl_3 slightly exceed rates of the other THMs. CHCl_3 is often the most abundant THM species and among the more toxic, thus, most attention has focused on this chemical. However, the fraction of each THM species volatilized will be similar.

Exposure estimates for THMs and other volatile chemicals in tap water should account for losses occurring during

storage, preparation, and serving. Self-reported or other estimates of tap water consumption used in risk assessments and epidemiological studies should discriminate between water that has been boiled and consumed as tea, coffee, and other hot beverages and all other types of tap water consumption. Based on three large U.S. and Canadian studies of adults (>20 years) reported in the U.S. EPA Exposure Factors Handbook (40), tea, coffee, and other hot beverages account for 37 to 67% of the total water intake. This suggests potentially large biases for exposure estimates based on total tap water ingestion that do not account for volatilization from hot beverages. Using the average hot beverage consumption across the three studies (48%), the individual dose from tap water consumption is equivalent to 1.14 L/day (assuming 1.04 L/day of water consumed cold with minimal loss of THMs, and 0.96 L consumed as a hot beverage with 90% loss), rather than the 2 L/day usually assumed. Thus, adult ingestion exposures that do not correct for volatilization overestimate exposure by nearly a factor of 2. (Persons under 20 years of age drink few hot beverages, thus corrections are smaller or not needed.) In consequence, other exposure pathways for THMs, e.g., inhalation during bathing, may account for a larger portion of the total THM dose than previously believed. While available literature estimates of inhalation and dermal permeation rates for THMs vary, inhalation exposures may approach or exceed the significance of that from tap water ingestion.

Limitations and Further Questions. The volatilization rates presented in this paper were designed to portray several common indoor situations. Other conditions may increase mixing, which was deliberately limited in the experimental protocol, and thus significantly enhance volatilization rates. Container shapes affect volatilization rates. The presence of an aerator on a faucet will result in additional volatilization that was not portrayed in the laboratory simulation. However, relatively small losses are expected from screens or aerators for THMs for cold or cool water, based on studies of compounds with higher Henry's law constants, e.g., toluene (25). Results in this paper are applicable to THMs in water. Potentially, THMs may sorb to solids or otherwise interact with substances in tea, coffee, and food, decreasing volatilization rates. Also, there is some evidence that THMs may be formed during tea preparation from precursors residual chlorine in the tap water and organic matter in the tea (41). While boiling is expected to reduce chlorine concentrations, the net effect is unknown.

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